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GROWTH AND CHARACTERIZATION OF PURE AND COBALT DOPED CALCIUM OXALATE MONOHYDRATE CRYSTALS

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ABSTRACT

Calcium oxalate is one of the major constituent of renal calculi. Calcium containing stones especially Calcium Oxalate Monohydrate (COM), Calcium Oxalate Dihydrate (COD), Calcium Oxalate Tri-hydrate (COT) and basic calcium phosphate, struvite, uric acid and cystine. The kidney stone is major health problem all over the world. Cobalt is widespread in the natural environment and can be formed as an effect of anthropogenic activity. The pure calcium oxalate and cobalt doped calcium oxalate monohydrate crystals were grown by single diffusion gel growth technique. The grown crystals were characterized by FTIR, XRD and SEM-EDX analysis.

KEYWORDS: CaOx, Silica gel, XRD, FTIR.

1. INTRODUCTION

Urinary stone disease is one of the ancient and general afflictions of humans. All over the world 12% of the population was suffering from such urinary stone problem due to global warming, modern life style and food habits. Calcium content is the most commonly occurring form of nephrolithiasis or urinary stone diseases. The most common forms of calcium crystals such as Calcium Oxalate Monohydrate (whewellite), Calcium Oxalate Dihydrate (weddllite) Calcium Oxalate Tri-hydrate and calcium phosphate as hydroxyapatite (HAP), brushite and octa-alcium phosphate (1-3). Calcium Oxalate has low solubility in water and crystallized in three hydrated forms COM, COD and COT. Calcium stone form to influence by food habit, environmental factors and due to like as calcium, sodium, protein, carbohydrates (4-7). Cobalt is an essential trace element in the human body into development of cells growth. Cobalt is the most used vitamin12 levels. Many authors have attempted to grow calcium oxalate monohydrate crystals by silica gel method. The growth and characterization of calcium oxalate monohydrate, calcium oxalate dehydrates and hydroxyapatite crystal by gel method (8). Investigations of the urinary stones showed large number of trace elements Cd, Pb, Zn, Mg, Sr, Cr, Mn, Ni, Co, Cu, Au, Ti, Bi etc. along with the main constituents (9). An increase in the level of the trace element in the body fluid leads to the crystal deposition which results in the development of kidney stones (10). Two different calcium oxalates types of urinary calculi, recovered after surgery were analyzed by Fourier Transform infrared spectroscopy, thermo gravimetric analysis, powder X-ray diffraction analysis, scanning electron microscopy and energy dispersive analysis of X-ray in order to determine composition, impurities and the type of other phases present in the calculi (11). The characteristics, dielectric properties and surface morphology of calcium oxalate monohydrate single crystals are grown in silica gel medium (12). The calcium hydrogen phosphate dehydrate crystal has been crystallized in silica gel technique (13). The Fourier Transform Infrared (FT-IR) results indicate that stones have different composition, namely calcium oxalate, calcium phosphate, carbonate apatite, magnesium ammonium phosphate and uric acids (14). In-vitro growth of calcium oxalate monohydrate crystal by single diffusion gel growth method in silica gel medium. The harvested crystals are characterized by Fourier Transform Infrared spectroscopy; X-ray diffraction and thermal analysis are studied (15).

In the present study has been made to growth of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystal in single diffusion gel method. The harvested crystals were characterized by FTIR, XRD, and SEM-EDX analysis.

2. MATERIALS AND METHODS

2.1 Crystal Growth

The growth of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystal was carried out in silica gel. All the chemicals used in this experiment are of AR grade. The borosilicate glass test tubes of 2.5cm diameter and 20cm length were used as crystallizing vessels. In a single diffusion gel method, gel was set by mixing sodium meta silicate solution of density 1.03g/cm^3 was adjusted to a pH of 6 by adding 5% glacial acetic acid **(16)**. Calcium chloride and cobalt chloride one of the reactants was incorporated inside the gel. After the gel was set an aqueous solution of oxalic acid with slowly added over the gel and the experiments were conducted at room temperature. Within a day, a white column of tiny crystals are formed. The growth was completed within a period of 21 days and harvested the crystals which are as shown in Fig 1(a) and 1(b). The harvested cobalt doped calcium oxalate monohydrate crystals are shown in Fig 1(c) and 1(d). Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, etc., have considerable effect on growth rates.

Table. 1. The optimum condition for the growth of cobalt doped calcium oxalate monohydrate crystal.

S. No	Parameters	Optimum condition
1	Density of sodium meta silicate	1.03gm/cm^{-3}
2	pH of gel	6
3	Concentration of $CaCl_2$	1 M
4	Concentration of $CoCl_2$	0.01M
5	Concentration of $C_2H_2O_4$	1 M
6	Gel setting period	2 days
7	Gel aging	1 month
8	Period of growth	21 days
9	Temperature	Room temperature

Fig. 1(a). Growth of pure CaOxM crystal

Fig. 1(b). The harvested pure CaOxM crystal

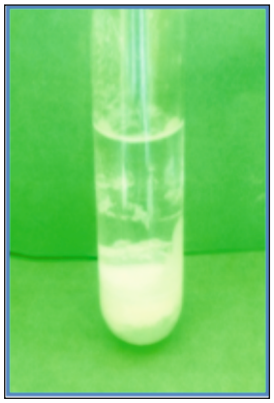

Fig 1.(c) Growth of CoCaoxM crystal

Fig.1.(d) The harvested CoCaoxM crystal

2.2 Characterization Techniques

FTIR spectrum is recorded by KBr pellet technique using Perkin Elmer FTIR spectrometer with the range 400-4000cm^{-1} is available at Centralised Instrumentation Science Laboratory, Department of Physics, St.Joseph College, Tiruchirappalli. Powder X-ray diffraction of the samples are carried out by EXPERT-PRO with CuKα radiation (=1.5418A^0) is available at Department of Physics, Alagappa University, Karaikkudi. The surface morphology of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystal was studied by JEOL, JSM 6390 SEM and the presence of elemental composition was calculated by OXFORD instruments TINCA pental FETX3 EDX method is available at Karunya University, Coimbatore.

3. RESULTS AND DISCUSSION

Gel method is used to grow pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystal. The above crystals are analysed by FTIR, XRD and SEM-EDX analysis.

3.1 Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals as shown in Fig 2(a) and 2(b). The spectrum shows various frequencies of vibrational modes. Each mode characterizes particular functional group identified from IR correlation chart (17). The vibrational modes of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate are presented in Table 2. In FTIR spectra, a strong band at 3431cm^{-1}, 3434cm^{-1} and 3063cm^{-1}, 3062cm^{-1} is due to asymmetric and symmetric OH stretching while an intense absorption band at 3262cm^{-1}, 3261cm^{-1} show inter molecular hydrogen bonded OH stretch. The absorption band at 1621cm^{-1}, 1612cm^{-1} and 1318cm^{-1} can be assigned to asymmetric and symmetric C=O stretching bands specific to the calcium oxalate monohydrate. The sharp band at 885cm^{-1}, 886cm^{-1} is due to C-C stretching vibrations which confirm the existence of oxalate group in calcium oxalate monohydrate. The sharp peaks at 781cm^{-1} is due to O-C=O and the wideband at 662cm^{-1}, 665cm^{-1} can be assigned to the bending modes of the water molecule. However, the peak at 516cm^{-1} 518cm^{-1} is assigned to the presence of metal-oxygen bond **(18).** Thus FTIR reveals that the growth of calcium oxalate monohydrate crystals was due to the presence of O-H stretching, C=O, C-C, O-C=O and M=O bonds.

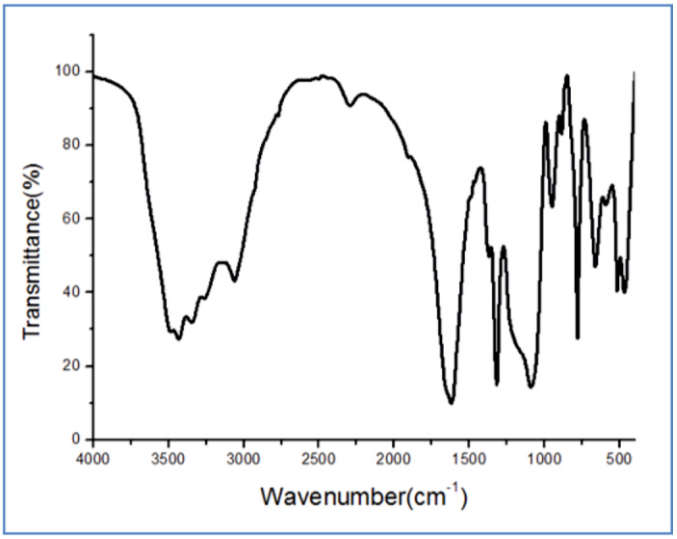

Fig.2 (a) FT-IR spectrum of pure calcium oxalate monohydrate crystals.

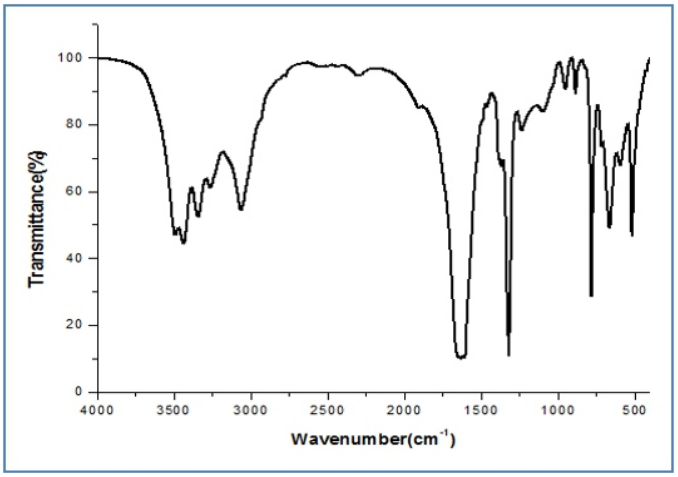

Fig. 2. (b) FT-IR spectrum of cobalt doped calcium oxalate monohydrate crystals

Table.2. FTIR wave numbers and vibrations assignments of pure and cobalt doped calcium oxalate monohydrate crystals.

Pure calcium oxalate monohydrate wave number in cm-1	Cobalt doped calcium oxalate monohydrate wave number in cm^{-1}	Vibrational band assignments
3431	3434	Asymmetric OH stretch
3063	3062	Symmetric OH stretch
3262	3261	Inter molecule H_2 bonded OH stretch
1621	1612	Asymmetric C=O stretch
1318	1318	Symmetric C=O stretch
1092	1098	Asymmetric C-O stretch
951	950	Symmetric C-O stretch
886	885	C-C stretch
781	781	O-C=O stretch
662	663	OH wagging
516	516	M-O bond

There are some additional peaks formed due to the process of doping some absorption peaks due to OH vibrations are changed because of the incorporation of dopant in the lattice. In the case of cobalt doped calcium oxalate monohydrate crystals of additional peaks are found at 1285cm^{-1} and 1462cm^{-1} which are attributed to the C=O stretching. These peaks are found to be present in the spectrum of cobalt doped calcium oxalate monohydrate confirms the presence of the element cobalt.

3.2 XRD Analysis

The powder XRD pattern was recorded using diffractometer system=XPERT-PRO X-ray diffractometer with CuKα radiation (=11.546A^0). The powder sample was scanned over the range 10^0 to 60^0 in at a rate of 1^0 per minute. Fig 3(a) and 3(b) shows the X-ray diffraction analysis of the pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate.

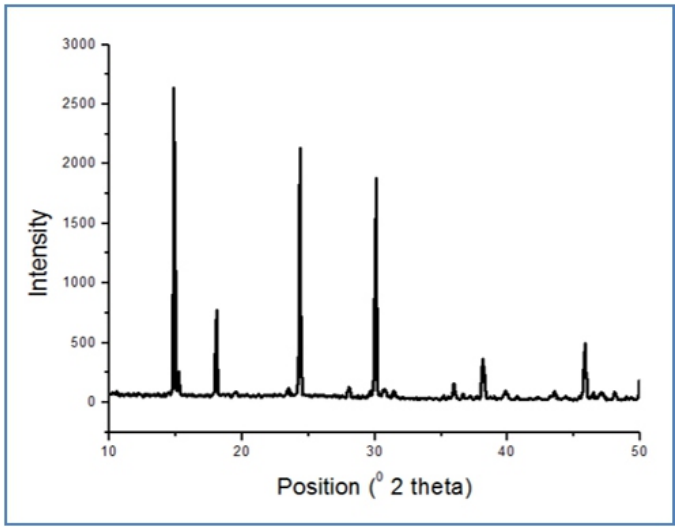

Fig. 3(a). X-ray diffraction analysis of pure calcium oxalate monohydrate crystal.

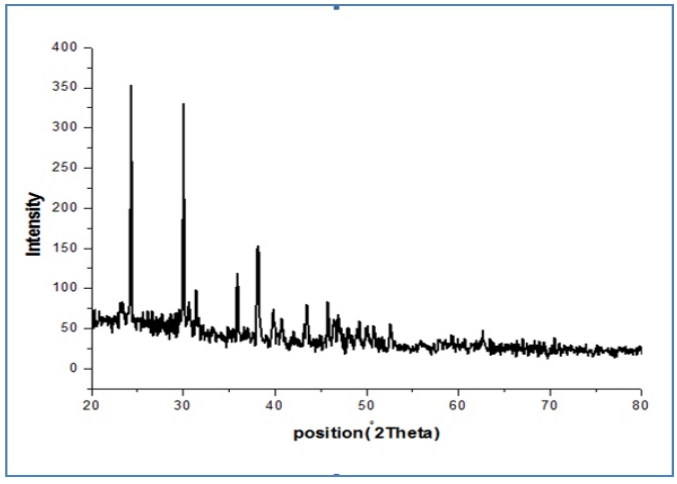

Fig 3(b) X-ray diffraction analysis of cobalt doped calcium oxalate monohydrate crystals.

The powder XRD analysis of the grown calcium oxalate monohydrate crystals was matched with the reported database using computer with PAN analytical software and result was matched with JCPDS File (14-0789). The indexed powder data for the cobalt doped calcium oxalate monohydrate crystals are presented in Table 3 and 4. From the collected XRD data, it is observed that from the cell parameters of both pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals belong to monoclinic system.

Table. 3. Powder X-ray diffraction analysis of pure calcium oxalate monohydrate crystals.

Std value			Observed value			hkl value
2θ	I/I_0	d-space	2θ	I/I_0	d-space	
14.927	100	5.94	14.886	100	5.95	-101
15.290	60	5.79	15.259	19	5.80	011
23.516	40	3.78	23.527	11	3.78	-112
24.366	100	3.65	24.366	63	3.65	020
30.084	80	2.96	30.075	66	2.97	-202
31.440	40	2.84	31.679	14	2.82	121
35.965	20	2.49	35.943	16	2.49	211
37.136	20	2.41	37.297	2	2.41	-213
38.150	60	2.35	38.184	28	2.35	031
39.782	40	2.26	39.833	11	2.26	014
40.796	40	2.21	40.763	6	2.21	-204
43.560	60	2.07	43.588	10	2.07	123
45.837	60	1.97	45.855	14	1.97	-303
46.509	40	1.95	46.496	10	1.95	132
46.963	40	1.94	46.959	9	1.93	222
48.076	40	1.89	48.064	4	1.89	230

Table. 4. Powder X-ray diffraction analysis of cobalt doped calcium oxalate monohydrate crystals.

Standard value			Observed value			hkl value
2θ	I/I0	d-space	2θ	I/I0	d-space	
14.927	100	5.93	14.861	100	5.96	-101
15.290	60	5.79	15.219	29	5.82	011
24.365	40	3.65	24.332	98	3.65	021
30.083	100	2.96	30.057	84	2.97	-202
31.439	80	2.84	31.511	12	2.83	121
35.964	40	2.52	35.913	27	2.50	211
38.148	20	2.35	38.168	37	2.35	031
39.780	20	2.26	39.808	13	2.26	014
40.795	60	2.25	40.723	10	2.21	-204
43.558	40	2.07	43.530	15	2.07	123
45.835	40	1.97	45.819	11	1.98	-303
46.507	60	1.95	46.539	9	1.95	114
48.074	60	1.89	48.028	6	1.89	230
49.323	40	1.84	49.106	5	1.85	510
50.282	40	1.81	50.069	6	1.82	-123
50.883	40	1.79	50.837	7	1.79	132

The peaks in the XRD patterns which were obtained slightly shifted due to the addition of dopants which indicates that the dopants have entered into the lattice of the crystal. It is seen that the X-ray pattern is almost similar indicating the presence of cobalt has not affected the crystalline nature of the sample (18).

3.3 Scanning Electron Microscope and Energy Dispersive X-ray analysis

The morphology of the pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals was studied by SEM as shown in Fig 4(a) and 4(b). The growth of pure calcium oxalate monohydrate crystals were obtained in different morphologies such as monoclinic, prismatic, hexagonal morphology. The cobalt-calcium oxalate monohydrate crystal appeared as monoclinic prismatic six sided platy shape morphology.

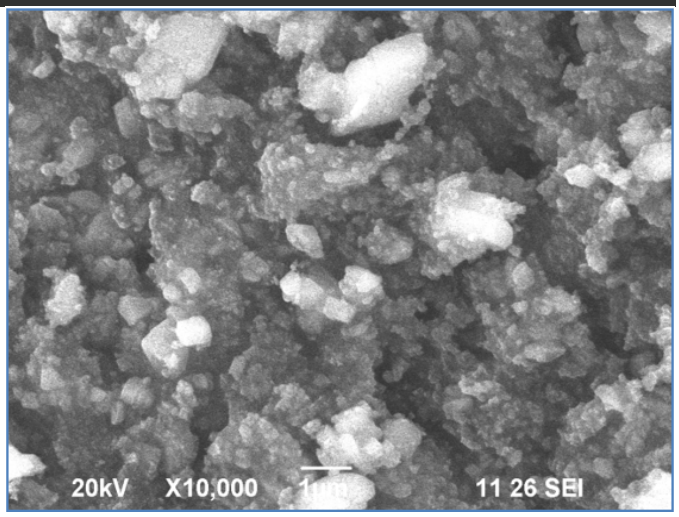

Fig. 4(a) SEM images of pure calcium oxalate monohydrate crystals.

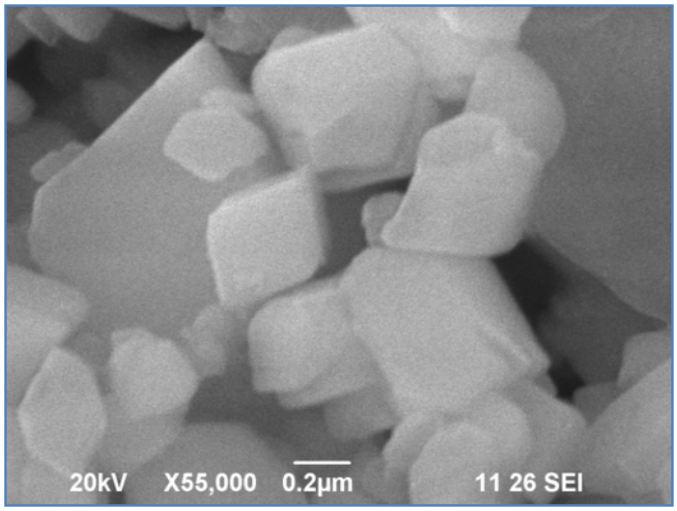

Fig. 4(b) SEM images of cobalt doped calcium oxalate monohydrate crystals.

It was found that, the structure of the grown crystals does not affect the morphology of the crystals by doping. The presence of calcium and cobalt quantitative elemental analysis were performed on the application of energy dispersive X-ray analysis of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals as shown in Fig 5(a) and 5(b).

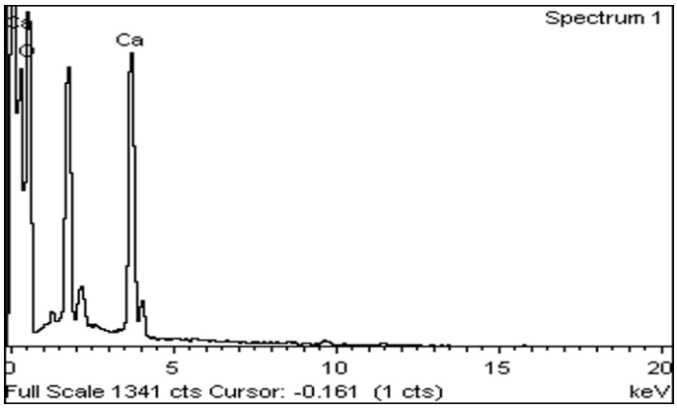

Fig 5(a) EDX spectrum of pure calcium oxalate monohydrate crystals.

Table 6(a) EDX analysis of pure calcium oxalate monohydrate crystals.

Element	Atomic weight%	Mass weight%
O	91.37	80.86
Ca	8.63	19.14
Total	100	100

The atomic percentage of present element O and Ca was found to be 91.37%, 8.63% are present in pure calcium oxalate monohydrate crystals.

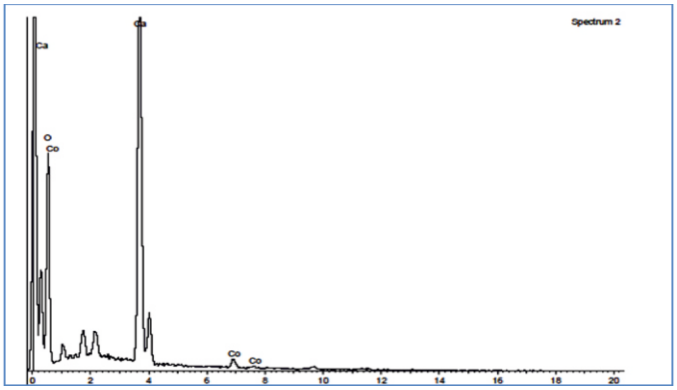

Fig.5. (b) EDX spectrum of cobalt doped calcium oxalate monohydrate crystals.

Table. 6(b). EDX analysis of cobalt doped calcium oxalate monohydrate crystals.

Element	Atomic weight%	Mass weight%
O	71.72	85.65
Ca	26.42	12.74
Co	1.86	0.61
Total	100	100

The atomic percentage of present element O, Ca, and Co was found to be 71.72%, 26.42%, and 1.86% are present in cobalt doped calcium oxalate monohydrate crystals.

CONCLUSION

Gel growth technique is used to grown urinary type of crystals. The crystalline structure was identified by XRD analysis. FTIR spectrum of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate confirmed the presence of functional groups. The SEM image shows surface morphology of the grown crystals and the energy dispersive X-ray analysis confirmed the cobalt doped calcium oxalate monohydrate.

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